

Open Research Online

The Open University's repository of research publications
and other research outputs

FTIR 2–16 micron spectroscopy of micron-sized olivines from primitive meteorites

Journal Item

How to cite:

Morlok, A.; Bowey, J.E.; Kohler, M. and Grady, M.M. (2006). FTIR 2–16 micron spectroscopy of micron-sized olivines from primitive meteorites. *Meteoritics and Planetary Science*, 41(5) pp. 773–784.

For guidance on citations see [FAQs](#).

© [\[not recorded\]](#)

Version: [\[not recorded\]](#)

Link(s) to article on publisher's website:

<http://www.ingentaconnect.com/content/arizona/maps/2006/00000041/00000005/art00010>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk



FTIR 2–16 micron spectroscopy of micron-sized olivines from primitive meteorites

A. MORLOK^{1, 2*}, J. BOWEY³, M. KÖHLER⁴, and M. M. GRADY^{2, 5}

¹Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

²Department of Earth and Planetary Sciences, Faculty of Science, Kobe University, Kobe 657-8501, Japan

³Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

⁴Institut für Planetologie, Wilhelm-Klemm-Str.10, 48149 Münster, Germany

⁵PSSRI, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

*Corresponding author. E-mail: morlok70@kobe-u.ac.jp

(Received 21 April 2005; revision accepted 28 January 2006)

Abstract—Infrared spectra of mineral grains from primitive meteorites could be useful for comparison with astronomical infrared spectra since some of their grains might be similar to those formed in the planet-forming disks around young stars or in the envelopes surrounding late-type stars. To assess the usefulness of meteorite spectra, olivine grains separated from primitive meteorites have been analyzed using FTIR microscope techniques in the 2–16 μm wavelength range. The sub-micron sizes of the grains made a complex preparation process necessary.

Five characteristic bands were measured near 11.9, 11.2, 10.4, 10.1, and 10.0 μm . The results of 59 analyses allow the calculation of band positions for meteoritic olivines as a function of their iron and magnesium contents. Comparison of the meteoritic results with astronomical data for comets and dust around young and old stars, which exhibit bands similar to the strongest infrared bands observed in the grains (at 11.2 μm), show that the spectral resolution of the astronomical observations is too low to ascertain the exact iron and magnesium (Mg:Fe) ratio of the dust in the 8–13 μm wavelength range.

INTRODUCTION

The ubiquity of dust (interstellar, circumstellar, interplanetary, cometary, and asteroidal) is an indication of its importance in a variety of astrophysical environments. Over the past few years, there has been increasing recognition that astrophysical dust is not simply a homogeneous mass of amorphous material, but frequently occurs as crystalline silicates (e.g., Waters et al. 1996). The most abundant minerals recognized are the Mg-Fe silicates, olivine, and pyroxene (Molster et al. 2002). These identifications have been based on the interpretation of strong features in the Fourier transform infrared (FTIR) spectra of astronomical dust, and IR spectroscopy is now a powerful tool that can relate astronomical data to laboratory-based studies of dust (Colangeli et al. 2003).

Mid-IR (between 10 μm and 18 μm) spectroscopy of a variety of galactic environments reveals smooth emission and absorption bands that have been associated with Si-O stretching and bending modes in amorphous silicates (see the review by Draine 2003). Controversially, Bowey and Adamson (2002) matched the gross properties of the astronomical profiles (the width and the wavelength of the

peak) with a mixture of crystalline silicates (the spectral features of which are narrow and highly structured) with a relatively small component of amorphous silicate. By this analysis, the breadth of the 10 μm features in the circumstellar disks surrounding young stars could be reproduced by a mixture of crystalline pyroxenes with varying stoichiometries (80% by mass) and amorphous silicates (20%).

Such an explanation may be more consistent with current interpretations of the far-infrared spectra of young and old stars with circumstellar dust shells and disks obtained with, for example, the infrared space observatory (Kessler et al. 1996). The narrow spectral emission features indicate the presence of crystalline silicates (Waters et al. 1996). Forsterite was first identified as an important component of some circumstellar dust environments based on the strength and position of narrow bands at 23.7 μm and 33.5 μm in the spectrum of the isolated Herbig Ae/Be star HD 100546 (Waelkens et al. 1996).

Many previous investigations have used terrestrial minerals and artificial glasses for calibration and spectral matching with astronomical data. Most published infrared transmission or absorbance spectra are obtained from bulk samples of natural and synthetic terrestrial materials using

workbench IR spectrometers (e.g., Jäger et al. 1998; Chihara et al. 2002; Koike et al. 2003). However, the compositional range of terrestrial minerals is restricted compared with that of their extraterrestrial counterparts, so in order to provide a more realistic set of mineral compositions for comparison with astronomical dust spectra, we are characterizing the IR signatures of silicate grains separated from primitive meteorites (e.g., Morlok et al. 2004). These minerals cover the compositional range of interest much better than the specimens of earlier studies.

Another purpose of this study was to investigate if olivines formed in non-terrestrial environments exhibit spectral differences compared to terrestrial or synthetic olivines. Since minerals in meteorites formed in environments closer to those of the dust observed by astronomers (and entirely different from terrestrial ones), their infrared spectra may provide better standards for calibration of astronomical spectra than material from terrestrial sources.

Extraterrestrial material has mainly been analyzed in the form of bulk samples of whole meteorites, usually in the visible/near-infrared range from about 0.3 to 2.5 μm (Chapman and Salisbury 1973; Johnson and Fanale 1973; Salisbury et al. 1975; Gaffey 1976). There is also a wealth of mid-infrared data from the bulk meteorites available (e.g., Zaikowski and Knacke 1975; Sandford 1984; Jones et al. 1989; Salisbury et al. 1991; Miyamoto 1992; Miyamoto and Zolensky 1994; Osawa et al. 2001). In contrast to bulk studies, there are only a few studies of specific mineral phases in meteorites, e.g., absorption measurements of presolar diamonds (e.g., Braatz et al. 2000) and sulphides (Keller et al. 2000, 2002) and reflectance studies of minerals in achondrites and ordinary chondrites (Bukanovska et al. 1998; Maras et al. 2001); Martian and carbonaceous meteorites (Cooney et al. 1998; Palomba et al. 2001). Microspectroscopic methods allow the measurement of grains as small as $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$; however, the practical limit is larger than this due to diffraction effects.

The spatial resolution makes it possible to obtain infrared spectra from specific areas within the fine-grained material that can be characteristic of primitive meteorites. It also allows analysis of very small amounts of separated material, e.g., single grains. Microspectroscopic methods have been applied to primitive planetary materials, including micrometeorites (Osawa et al. 2001), interplanetary dust particles (IDPs) (Keller and Flynn 2003; Molster et al. 2003), and glass with embedded metal and sulphides (GEMS) within IDPs (Bradley et al. 1999), as well as bulk meteorites (Raynal et al. 2000) and some meteorite components (Dalton and Bishop 2003; Moroz et al. 2005).

This paper is part of a systematic survey of FTIR and optical spectra from minerals in meteorites. Our aim is to compile a comprehensive database of spectra acquired by microspectroscopic FTIR techniques for comparison with spectra of dust obtained from astronomical sources. We have

selected material from primitive type 3 chondrites for study. This group of meteorites (and their mineral components) have suffered minimal thermal or aqueous alteration since formation of their parent bodies in the young solar system. This paper focuses on olivines, which is one of the most common of meteoritic silicates. Olivine occurs in several locations within primitive meteorites: in chondrules, in fine-grained inter-chondrule matrix, in high-temperature aggregate, and as isolated grains.

SAMPLES AND TECHNIQUES

Minerals of the olivine group have orthorhombic symmetry. The SiO_4^{4-} tetrahedra are isolated in the structure, linked by cations (Fe^{2+} , Mg^{2+} , rarely Ca^{2+} or Mn^{2+}) in octahedral positions. The generic formula is $(\text{X},\text{Y})_2\text{SiO}_4$, with a solid solution between the magnesium and iron rich end-members forsterite (Fo_{100} ; Mg_2SiO_4) and fayalite (Fo_0 ; Fe_2SiO_4). In other words, the cation positions in the structure can be filled with iron and magnesium in all possible ratios (Deer et al. 1992). Olivines from primitive meteorites may contain significant concentrations of other cations, e.g., chondrule olivines from slightly metamorphosed (<3.7) chondrites may contain up to $\sim 0.7\text{ wt}\%$ CaO , $\sim 0.6\text{ wt}\%$ Al_2O_3 , $\sim 0.5\text{ wt}\%$ MnO , and $0.9\text{ wt}\%$ Cr_2O_3 (Brearley and Jones 1998).

In the following, the iron and magnesium (Fe/Mg) ratio in olivines is expressed as the forsterite content, calculated from the atomic% of Fe and Mg in the measurements. Of special interest are systematic band shifts in relation to forsterite contents. Effects of varying cation radii on band positions have been observed previously. With increasing magnesium content, most bands shift to higher wave numbers (lower wavelengths) (e.g., Tarte 1965; Burns and Huggins 1972; Farmer 1976; Chihara et al. 2002; Morlok et al., Forthcoming). The mid-infrared bands featured in this study are ν_1 and ν_3 stretching modes of the SiO_4 tetrahedron in the olivine structure; these bands have wavelengths around $10\text{ }\mu\text{m}$ – $12\text{ }\mu\text{m}$, and occur in the centre of the detector range of the FTIR microscope.

Sample Selection

The typical range of forsterite content in olivines from primitive chondrites is Fo_{60} to Fo_{100} . Different meteorite groups have different forsterite compositions, making complete coverage of the whole forsterite range with one meteorite group difficult. We therefore selected five different meteorites, representing five separate parent asteroids (the sample numbers in brackets are those of the collection at the Natural History Museum): the LL3.6 ordinary chondrite Parnallee (BM34729), the H/L3.6 Tieschitz (BM1975,M.11), the H3.8 Dhjala (BM1976, M12), the CV3.3 carbonaceous chondrite Vigarano (BM1920, 347), and the CO3.3 carbonaceous chondrite Ornans (BM42474). All these

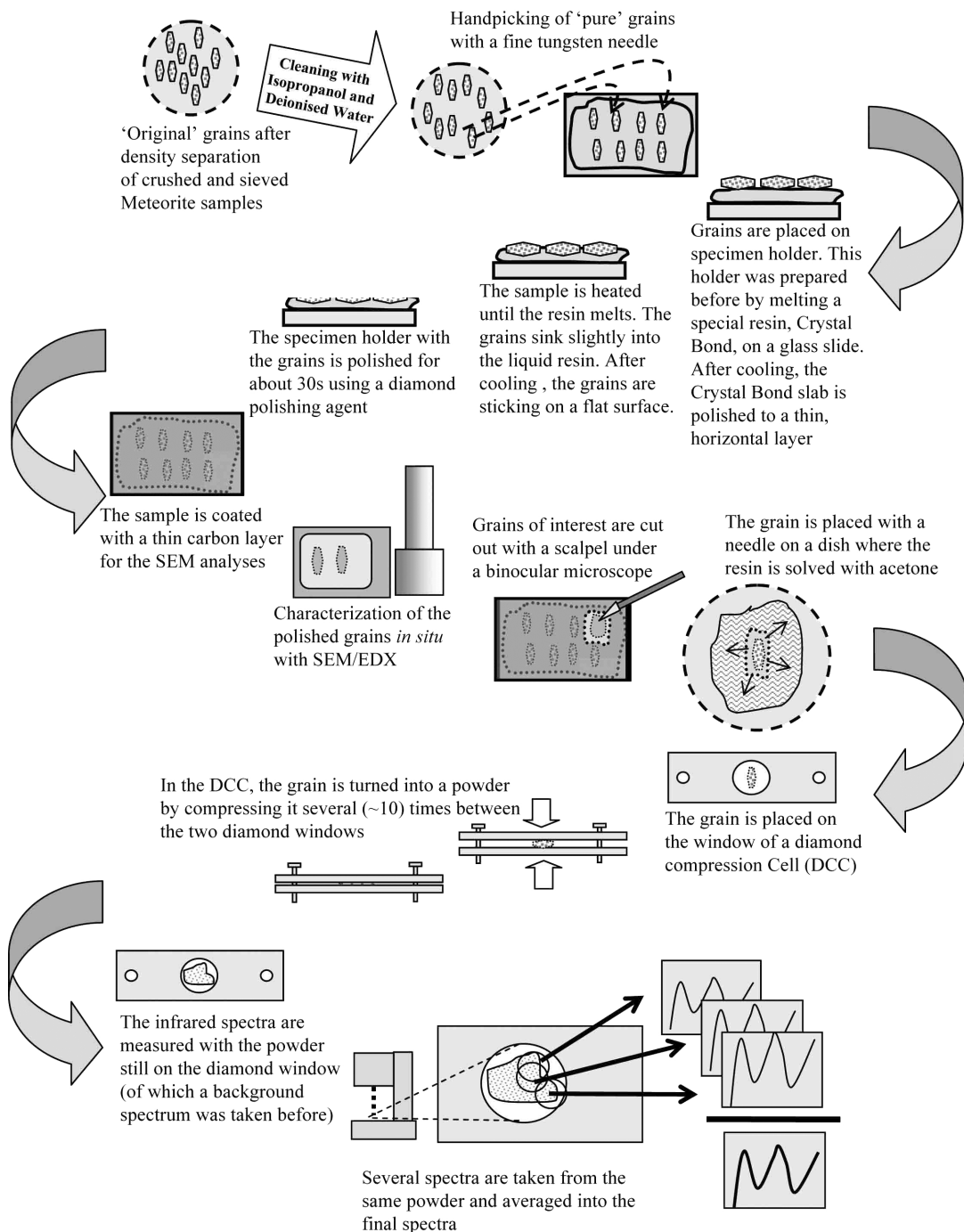


Fig. 1. The sample preparation procedure used for mineral grains in this study.

meteorites are falls that were collected shortly afterward, thus minimizing effects from terrestrial contamination or weathering.

The five meteorites are almost unshocked, with shock stages ranging from S1 to S2 (i.e., they have experienced shock pressure <10 GPa) and are of low petrologic type. The selected meteorites are thus little altered by heat and shock from the original dust from which they formed.

Sample Preparation and Characterization

Figure 1 depicts the stages that were followed for the analysis of individual mineral grains. Mineral separates had been obtained from the meteorites by density and magnetic separation techniques. Some grains had been prepared using the chlorination method of Moss et al. (1967). The mineral fractions (mostly in sizes <100 μm) were washed with

isopropanol or alcohol and deionized water and then dried. Single grains were picked out from the sample reservoir using a tungsten needle under a binocular microscope. The selected grains were partially embedded in a soluble resin (Crystal Bond™), then gently polished for ~30s, using a diamond polishing agent in order to create as flat a surface as possible on the partially embedded grains. The grains were then carbon-coated for compositional analysis.

Prior to infrared measurement, the mineralogy and mineral chemistry of each grain was determined by analytical scanning electron microscopy (SEM) using the Jeol 5900LV ProbeSEM at the Natural History Museum. Probe current was 2 nA at 20 keV. Appropriate natural and synthetic standards were used for calibration. Traditionally, compositional analyses are undertaken on polished flat 30 μm thick sections of meteorite. Because we were measuring individual grains that would also be examined in the IR microscope, this procedure was not possible. As shown in Fig. 1, the grains were mounted in a soluble resin that precluded extended polishing, and so in most cases no perfectly flat or even surfaces could be created. This resulted in analytical measurements where a sum of 100 wt% of all elements was not achieved. Mineral compositions with totals $100 \pm 25\%$ were taken and the elements were normalized to achieve totals of 100%. This is the usual procedure for unpolished, irregular grain mounts. Minerals were therefore characterized on the basis of their stoichiometry. As a measure of the “purity” of a grain, we used only grains where the normalized silicon content was within 5% the ideal stoichiometry (Deer et al. 1992). As an additional limit, only specimens where the normalized sum of all cations fell within 5% of the ideal stoichiometry of an olivine were used. Grains that were identified as clearly heterogeneous using their backscattered electron (BSE) image have been discarded. Olivine composition histograms for each meteorite, showing the internal range of forsterite content, are given in Fig. 2; the olivines extended over a range of compositions from Fo₆₀ to Fo₁₀₀.

Infrared Analyses

For spectral analyses, the grains were separated from the specimen mount using a scalpel under a binocular microscope. The grains were placed on a small dish where they were cleaned of the surrounding resin and carbon coating with propan-2-one. Following separation, the samples were crushed to a fine-grained, sub-micron powder using a diamond compression cell (DCC). The DCC accessory consists of two steel bars with small (2 mm) diamond windows. The sample was placed on the first window bar and the second was placed over it. Using two screws, the bars were pressed together and the sample flattened and ground to a very fine powder (<1 μm). This method has been proven to produce results very similar to the “classic” transmission

techniques using KBr pellets. Comparisons of these techniques can be found in Hofmeister 1997; Osawa et al. 2001; Morlok et al., *Forthcoming*).

Infrared transmission/absorption measurements were made with a Perkin Elmer AutoIMAGE FTIR microscope and Spectrum One FTIR system using a Mercury Cadmium Telluride (MCT) detector. Spectra were taken in the wavelength range from 2.5 μm to 16.6 μm using a resolution of ~0.1 μm (4 cm^{-1}) at midrange. The aperture size used was 50 $\mu\text{m} \times 50\text{ }\mu\text{m}$. There were no features of interest in the spectra below 8 μm , and so only data from wavelengths above 8 μm are plotted in the figures. Before a grain was compressed, a background spectrum was taken from the diamond window on which the grain was supported. To minimize the impact of sampling artefacts (e.g., Hofmeister et al. 2000), spectra were taken of several spots on the diamond window and an averaged spectrum calculated. Averaged spectra for all the individual grains are given in Fig. 2. More information about the techniques and sampling methods used, as well as potential artefacts, can be found in Morlok et al. (*Forthcoming*).

The small amounts of material occasionally resulted in weak spectra. Absorption was rarely above 0.15 A (or below ~70% transmission), leading to a low signal/noise ratio. When necessary, to distinguish weak bands from noise, we compared several spectra and omitted obvious artefacts.

RESULTS

Examples of the spectra are shown in Fig. 3, where the wavelength range of the major bands is shown. There were five peaks in most of the spectra that could be assigned to various stretching modes. The positions of these bands can be used to characterize the olivine composition. Most of the bands are asymmetric Si-O stretching vibrations (ν) within the SiO₄ tetrahedron; they are assigned to specific modes according to Hofmeister (1987) and Hofmeister et al. (1989). Figure 4 shows the band positions relative to the forsterite content of the grains.

There is one very strong band at ~11.2 μm (band 2) (Fig. 3) in the wavelength range analyzed in this study. Bands 1 (at ~12 μm), 4 (10.1 μm), and 5 (10 μm) are much weaker, but usually clearly recognizable. Band 3 (10.4 μm) is weak and sometimes absent, while a sixth band (at ~9.5 μm) occurs in the spectra of only four grains, and is not shown in any of the figures. Several spectra exhibited a weak additional feature between bands 2 and 3 that can be seen in some of the individual spectra plotted in Fig. 2. Due to its rarity, this peak was not given a band assignment; we suspect it may have an orientational dependence.

Linear least squares fits of the peak wavelength of each mode as a function of composition for the Fo₆₀–Fo₁₀₀ range measured were obtained for bands 1 to 5 and the results are presented in Table 1. More than 68% of the results for bands

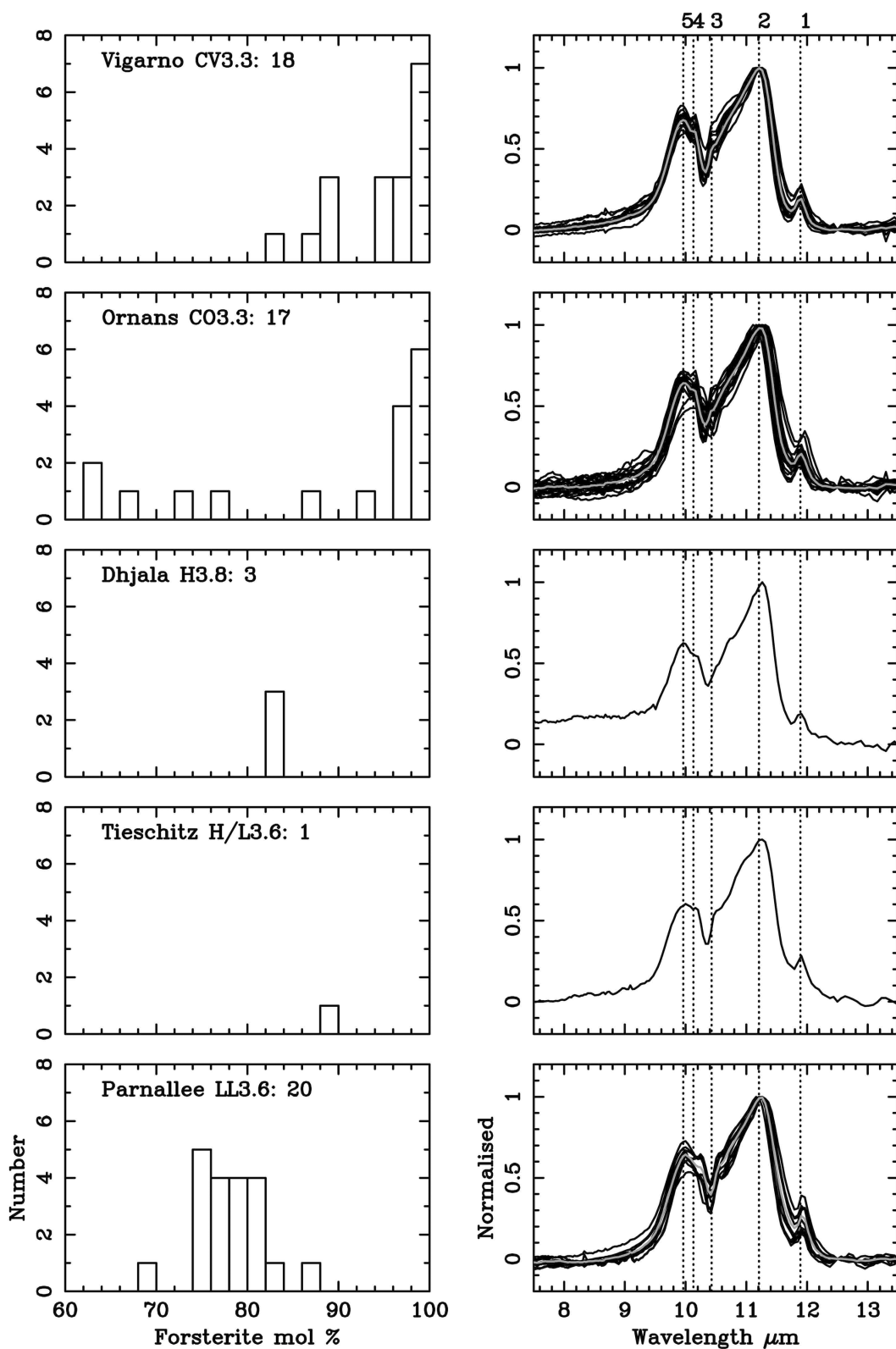


Fig. 2. Histograms of the sources for the mineral grains used in this study and their forsterite content. Generally, the whole range in composition from ~60 to 100% forsterite is covered without significant gaps. The accompanying spectra are summaries of all spectra obtained from each grain in the samples: black curves are representative spectra for each olivine composition, and grey curves are the average of the individual spectra.

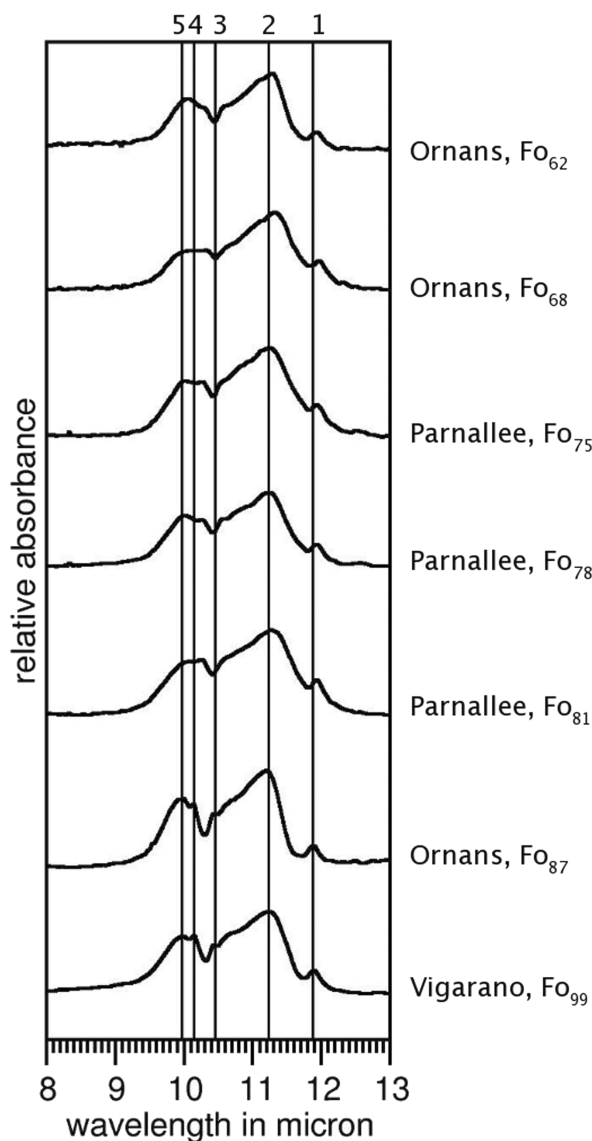


Fig. 3. Representative infrared spectra of the olivines analyzed in this study with forsterite contents from Fo_{62} to Fo_{99} . The vertical lines give the band position of the major bands calculated from the regression lines for Fo_{99} .

1 to 5 are within $\pm 0.1 \mu\text{m}$ of the regression lines, implying that the standard deviation (1σ) falls into this range. The correlation between composition band positions ranges from 0.56 (average) for band 2 to 0.94 (very good) for band 4 (Table 1). Bands 1 and 2 have shallower slopes than bands 3 to 5. Given that the relationship is linear over the Fo_{60} – Fo_{100} range, it is possible to extrapolate to the Fe-rich (i.e., $x \rightarrow 0$) end of the solid solution series (see Koike et al. 2003; Tarantino et al. 2003). However, there are exceptions to this (see the “Discussion” section).

While there are abundant data for olivine in the literature, we only included results in the diagram when the specific forsterite content was given (Hofmeister et al. 1997; Jäger

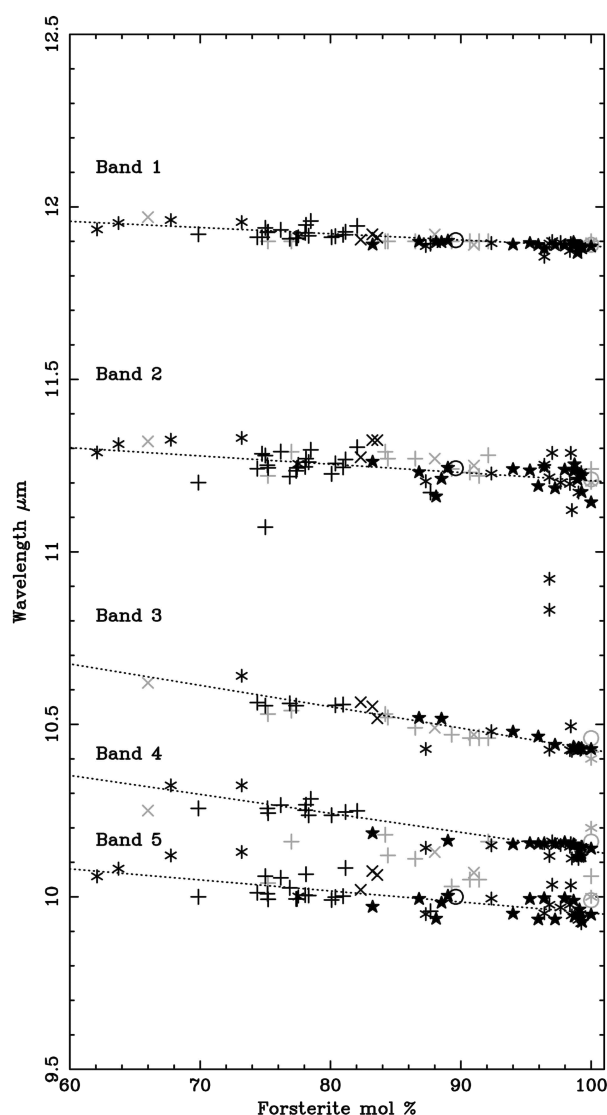


Fig. 4. An overview of the band position of the strongest infrared bands of the forsterite grains plotted versus their forsterite contents. Black symbols are data from this study: Parnallee (+), Ornans (*), Vigarano (O), Tieschitz (o), and Dhjala (x). Literature data has grey symbols: Koike et al. (2003); (+), Jäger et al. (1998); (*), Hofmeister (1997) (o), and Salisbury et al. (1992) (x). The continuous lines are least squares fits calculated for each band.

et al. 1998; Salisbury et al. 1992; Koike et al. 2003). Generally, our results are in good agreement with literature data when the range from Fo_{60} – Fo_{100} is compared. The majority of literature results fall into a $\pm 0.1 \mu\text{m}$ range of the regression line from a given band calculated from our data (Fig. 4). A band found in Koike et al. (2003) at $9.2 \mu\text{m}$ (Fo_{100} – $\text{Fo}_{39.5}$) was not found in our results, another at $9.5 \mu\text{m}$ (Fo_{100} – $\text{Fo}_{84.4}$) occurred only in four of our spectra. Further usually weak bands found occasionally by Jäger et al. (1998) for Fo_{100} at $9.3 \mu\text{m}$, $13.6 \mu\text{m}$, $13.8 \mu\text{m}$, and $14.6 \mu\text{m}$ also have no equivalent in this study. Another weak band at $10.8 \mu\text{m}$ (Fo_{94})

Table 1. Fitted wavelengths of observed bands 1–5, where $x = \text{Mg}/(\text{Fe} + \text{Mg})\%$.

Band (mode)	Number of grains (Total of 59)	Least squares fit (Fo_0 when $x = 0$)	R	Fo_{60} $\lambda/\mu\text{m}$	Fo_{100} $\lambda/\mu\text{m}$
1 (ν_1)	59	$\lambda = -0.0018x + 12.066$	0.83	11.96	11.89
2 (ν_3)	59	$\lambda = -0.0024x + 11.446$	0.56	11.30	11.21
3 (ν_3)	31	$\lambda = -0.0062x + 11.047$	0.93	10.68	10.43
4 (ν_3)	40	$\lambda = -0.0055x + 10.682$	0.94	10.35	10.13
5 ($\nu_3?$)	56	$\lambda = -0.0032x + 10.273$	0.70	10.07	9.96

is close to the unassigned bands of our data from Vigarano (Fig. 4). The above bands in the range below $\sim 9.5 \mu\text{m}$ are possibly overtones (Hofmeister 1987; Bowey and Hofmeister 2005). These are usually very weak bands approximately one–one-hundredth the strength of the fundamental bands, and so probably not recognizable in our microscope spectra of crushed micron-size grains. Also the missing features at longer wavelengths are probably too weak to be found with our technique.

DISCUSSION

Bands 4 and 5

The only significant difference in the compositional range from Fo_{60} – Fo_{100} between the $10 \mu\text{m}$ spectra of terrestrial and meteoritic olivines is that bands 4 ($10.1 \mu\text{m}$) and 5 ($\sim 10.0 \mu\text{m}$) are merged to form a single peak in many of the terrestrial spectra so that many of the literature peaks in Fig. 4 appear between the fits to the two meteoritic features.

A comparison of the entire Fo_{00} – Fo_{100} range of the literature data with the fits to the meteoritic bands in Fig. 5 shows the presence of two peaks in the studies by Hofmeister (1997), Jäger et al. (1998), and Koike et al. (2003), but the absence of band 5 in the spectra obtained by Salisbury et al. (1992). In Koike et al. (2003), results confirming band 5 chiefly fall into the range between Fo_{40} and Fo_{80} , while band 4 is represented by bands at the iron and magnesium rich ends of the compositional range.

These discrepancies and scatter in the measurements could be due to the similar band strengths of the two peaks and the small wavelength increment between the two bands ($\sim 0.2 \mu\text{m}$ at high Fo contents), which makes it difficult to resolve the pair in the spectra of powders. Two features (parallel to the y axis) are found in oriented single crystal measurements by Hofmeister (1987). Theoretical studies of spectra oriented along crystallographic axes have strong feature along x-axis, but along the other two axes (Morlok et al., Forthcoming). No equivalent orientation effects were obtained for the other bands observed in this study.

Fitted Band Positions in Meteoritic and Terrestrial Studies

We have measured the spectra of those meteoritic grains with compositions ranging between Fo_{60} and Fo_{100} , while the

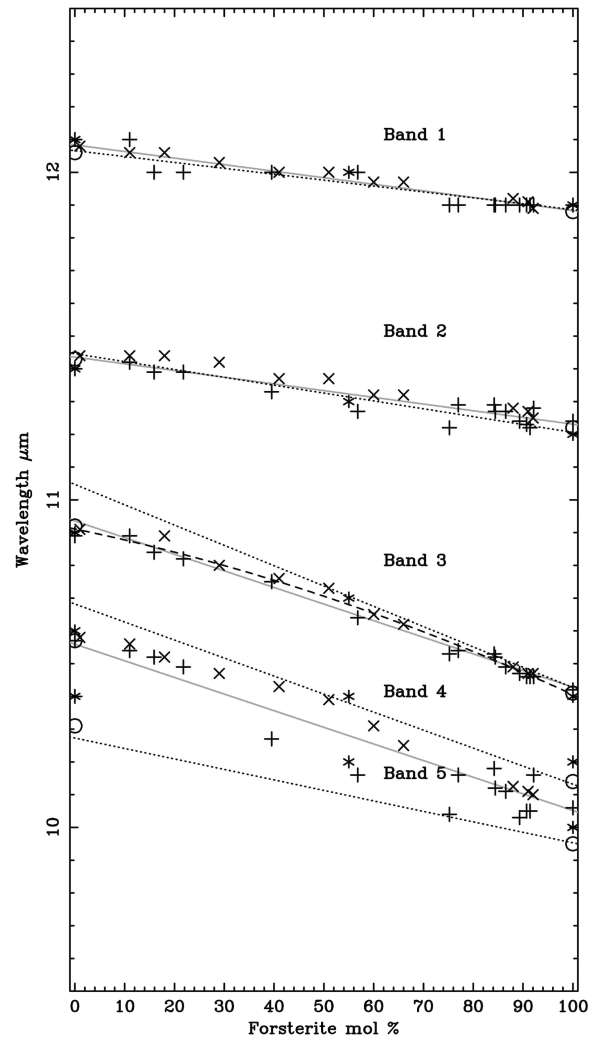


Fig. 5. A comparison of regression lines for bands this study (grey, continuous line, calculated from data between Fo_{60} and Fo_{100}) with literature from Fo_0 to Fo_{100} (black lines). The black symbols indicate band positions and are the same as the grey symbols in Fig. 4.

terrestrial studies measured spectra in the Fo_{00} – Fo_{100} range. Fits from this study are compared with fits to the literature data for the whole range of olivine composition from Fo_{00} – Fo_{100} (Table 2 and Fig. 5). The table lists separate fits to the data from each study and a fit to the entire published data set to avoid statistical bias due to the differing number of analyses obtained in each laboratory study. Bands 4 and 5

Table 2. A comparison of least squares fit for the meteoritic grains and of the literature data (Koike et al. 2003; Jäger et al. 1998; Hofmeister 1997; Salisbury et al. 1992) over the Fo_{00} to Fo_{100} range.

Bands	1	2	3	4	5	4 + 5
This study	$-0.0018x + 12.066$	$-0.0024x + 11.446$	$-0.0062x + 11.047$	$-0.0055x + 10.682$	$-0.0032x + 10.273$	$-0.0028x + 10.325$
Koike et al. (2003)	$-0.0020x + 12.078$	$-0.0018x + 11.414$	$-0.0050x + 10.923$	$-0.0056x + 10.596$	$-0.0047x + 10.419$	$-0.0050x + 10.529$
Jäger et al. (1998)	$-0.0020x + 12.103$	$-0.0020x + 11.403$	$-0.0050x + 10.922$	$-0.0040x + 10.606$	$-0.0040x + 10.406$	$-0.0040x + 10.506$
Hofmeister (1997)	$-0.0018x + 12.060$	$-0.0021x + 11.430$	$-0.0051x + 10.920$	$-0.0043x + 10.570$	$-0.0036x + 10.310$	$-0.0040x + 10.440$
Salisbury et al. (1992)	$-0.0020x + 12.087$	$-0.0022x + 11.465$	$-0.0052x + 10.958$	$-0.0055x + 10.624$		
All literature			$-0.0051x + 10.935$ or $-1.9 \times 10^{-5}x^2 - 0.00311x + 10.911$			
$\text{Fo}_{00}\text{--}\text{Fo}_{100}$	$-0.0020x + 12.083$	$-0.0020x + 11.436$				$-0.0051x + 10.559$
All literature						
$\text{Fo}_{60}\text{--}\text{Fo}_{100}$			$-0.0059x + 11.000$			

Note: The forsterite range for Koike was 100, 92.1, 91.4, 90.7, 89.3, 86.5, 84.4, 77, 75.2, 56.8, 39.5, 21.8, 15.9, 11.0, and 0.0 with a spectral resolution of 1 cm^{-1} . The range for Jäger was 100, 55, and 0. The range for Hofmeister was 100 and 0, and the range for Salisbury was 92, 91, 88, 66, 60, 51, 41, 29, 18, 11, and 1 (4 cm^{-1}). Band positions have been taken directly from studies. The combined fit excludes the Jäger Fo_{94} data due to possible sample contamination.

were fitted together since the spread of data in the Fo_{60} – Fo_{100} range made it difficult to distinguish both peaks.

Within the experimental uncertainties, the fits to bands 1 and 2 are the same for the terrestrial and meteoritic samples, irrespective of the differences in compositional range.

However, the fitted position of band 3 is much steeper in this study than it is for the published terrestrial studies. Since there is little difference between the meteoritic and terrestrial band positions plotted in Fig. 4 and fits to the published Fo_{60} – Fo_{100} data are very similar to the meteoritic results, we conclude that the difference in our results is due to the smaller compositional range. The slope of the fit to band 3 is shallower for olivines with more Fe (i.e., Fo_0 – Fo_{60}) than it is for the more Mg-rich grains. A better match to the entire range of the terrestrial data is produced by the quadratic expression given in Table 2. The fit to the combination of band 4 + 5 matches meteoritic band 4 more closely than band 5; this result is consistent with the larger number of peaks identified in the Salisbury et al. (1992) study.

Comparison with Astronomical Observations

The spectral properties of meteoritic olivines are compared with astronomical observations in Fig. 6. Mid-IR (10 μm and 18 μm) spectroscopy of astronomical dust in a variety of galactic environments reveals smooth absorption and emission bands that have been associated with Si–O stretching and bending modes in amorphous silicates, respectively, since the spectral features of crystalline silicates are narrow and highly structured. In contrast, longer-wavelength (20–100 μm) spectra of newly formed oxygen-rich circumstellar dust indicate the presence of crystalline silicates, principally, end-member forsterite (e.g., Waelkens et al. 1996) and pyroxenes (Molster et al. 2001).

Observations of distinctive crystalline features in the 8–13 μm range are rare, and when they are observed, they are principally identified with olivine because of the strength of the feature at $\sim 11.2 \mu\text{m}$. Spectral identification of crystalline silicates from ground-based telescopes is hampered by the presence of strong 9.4–9.8 μm absorption features resulting from ozone in the Earth's atmosphere and rapid changes in the atmosphere's opacity because of fluctuations in the proportions of water vapor. 10 μm observations of objects with far-infrared forsterite bands are frequently affected by the presence of strong narrow features identified with polyaromatic hydrocarbons which occur a range of wavelengths close to 7.7 μm , 8.7 μm , 11.0 μm , and 11.3 μm (e.g., Molster et al. 2001). The minerals identified in the far-infrared are unlikely to be seen at 10 μm because they have very low emission temperatures (~ 100 K) compared with 200–600 K typical of 10 μm silicate emission.

Olivine was first distinguished in the 10 micron spectrum of comet Halley (Bregman et al. 1987; Campins and Ryan 1989) and several other comets. Recently, olivine has been identified in the 10 μm spectra of comet Hale-Bopp (e.g.,

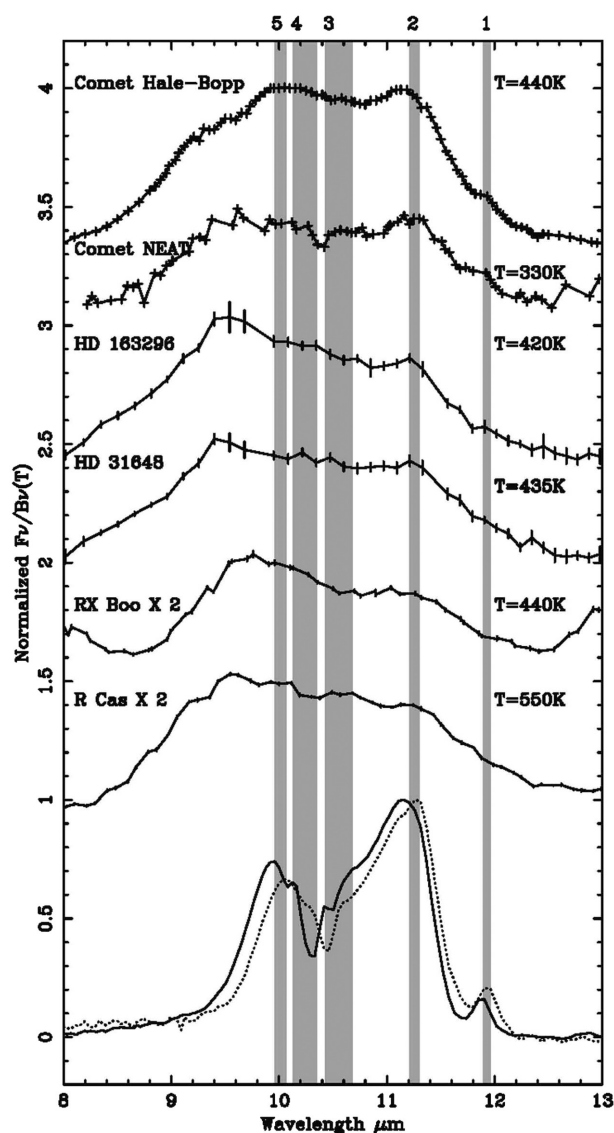


Fig. 6. A comparison of Fo_{100} (solid curve) and Fo_{60} (dotted curve) meteoritic grains with the astronomical emission features of: comets Hale-Bopp and C/2001 Q4 (NEAT) observed by Hanner et al. (1997) and Wooden et al. (2004), respectively; debris disks surrounding the pre-main sequence stars HD 163296 and HD 31648 (Sitko et al. 1999) and the circumstellar dust shells of post-main sequence oxygen-rich AGB stars R Cas and RX Boo (Speck et al. 2000). The grey bars indicate the fitted band positions of the measured Fo_{60} – Fo_{100} meteoritic grains. The astronomical flux (F_v) spectra have been divided by a black body ($B_v(T)$) of temperature T , where T is chosen so that the scaled flux of the black body is equal to that observed at 8 μm and 13 μm . All spectra are normalized to unity at their peak wavelength, except for the R Cas and RX Boo spectra, which have been multiplied by two in order to show off the contrast in their features. Offsets in the y-axis from the bottom are 0, –0.5, 0, 0.5, 1.5, 2.0, 2.5, and 3.0, respectively. The horizontal bars represent the band positions for a given band over the whole range from Fo_0 to Fo_{100} calculated from the regression lines.

Hanner et al. 1997) and the comet C/2001 Q4 (NEAT) (Wooden et al. 2004) as they entered the inner solar system.

As distance from the sun decreases and the cometary tail develops, features start to appear in the spectrum. Weak bands at 10.0 μm , 11.2 μm , and 11.9 μm that corresponding to the wavelengths of olivine peaks 5–4, 2, and 1, respectively, are superimposed on the broad 8–13 μm emission feature of comet Hale-Bopp, and bands 1 and 2 are seen in the noisier spectrum of comet C/2001 Q4 (NEAT).

Olivine has also been identified in the debris disks surrounding the pre-main sequence stars, for example, HD 31648 and HD 163296, by means of the 11.2 μm feature in their emission spectra (Fig. 6) (Sitko et al. 1999). We also suggest that olivine might contribute to the spectra of the oxygen-rich dust shells of the post-main sequence asymptotic giant branch (AGB) stars Cas and RX Boo, as indicated by the presence of an 11.2 μm feature in the spectra published by Speck et al. (2000), though this is tentative because the observed features are very broad in comparison to the laboratory features.

Unfortunately, the precise olivine composition cannot be determined from the 8–13 μm astronomical spectra because the compositional wavelength shifts in bands 1 and 2 are too small in comparison to the resolution of the astronomical instruments. It should also be noted, though, that there are other factors in addition to forsterite content that can cause peak shifts. Bowey et al. (2001) investigated shifts in band positions for the 15 to 85 μm range in olivines and pyroxenes at low temperatures (<3.5 K). However, changes for bands the mid-infrared are small (<0.2 μm) and an extrapolation to the 10 μm range suggests that the shifts would be <0.1 μm , e.g., Day (1976). Variations in grain size and shape are also commonly invoked as a source of differences between astronomical and laboratory measurements (Bohren and Huffman 1983).

CONCLUSIONS AND OUTLOOK

Infrared spectra of mineral grains from primitive, unequilibrated meteorites could be more useful than terrestrial olivines for comparison with astronomical infrared spectra, since it is expected that meteoritic grains would be similar to those produced in planet-forming disks around young stars, main-sequence stars, or in envelopes surrounding late-type stars. We find that the mid-infrared band positions of extraterrestrial olivine grains are similar to values for terrestrial and synthetic standards documented in earlier studies. In addition, the smaller compositional increments compared to earlier studies (Salisbury et al. 1992; Hofmeister et al. 1997; Jäger et al. 1998; Koike et al. 2003) allow an accurate determination of compositional trends at least in the compositional range from Fo₆₀–Fo₁₀₀. For meteoritic grains with forsterite compositions of 60–100%, five resonances in the IR spectra were measured at ~11.9 μm , 11.2 μm , 10.4 μm , 10.1 μm , and 10.0 μm ; the 10.0 and 10.1 μm features are not usually resolved in published studies

of bulk powders in this range of composition. The results of 59 analyses allow the calculation of “ideal” band positions for meteoritic olivines as a function of their iron and magnesium contents. Comparison of the meteoritic results with astronomical data for comets and dust around young and old stars that exhibit bands similar to the strongest IR-resonance observed in the grains (at 11.2 μm) show that the spectral resolution of the astronomical observations is too low to ascertain the Mg:Fe ratio of the dust in the 8–13 μm wavelength range. The astronomical spectra probably represent a combination of many grain types so that olivine may not be the only material that matches the observations.

Acknowledgments—We thank R. F. Symes and R. Hutchison for the mineral separates. Many thanks to G. Jones (NHM) for his guidance during the establishment of the FTIR system. Financial support from the PPARC to A. M., J. E. B., and M. M. G., and from the EU Marie Curie Programme for MK is gratefully acknowledged. This paper is IARC Contribution No. 2005-15. Reviews by G. J. Flynn and an anonymous reviewer, as well as the comments of Associate Editor C. Pieters helped to considerably improve the paper.

Editorial Handling—Dr. Carlé Pieters

REFERENCES

- Bohren C. F. and Huffman D. R. 1983. *Absorption and scattering of light by small particles*. New York: Wiley. 530 p.
- Bowey J. E. and Adamson A. J. 2002. A mineralogy of extrasolar silicate dust from 10 μm spectra. *Monthly Notices of the Royal Astronomical Society* 334:94–106.
- Bowey J. E. and Hofmeister A. M. 2005. Overtones of silicate and aluminate minerals and the 5–8 μm ice bands of deeply embedded objects. *Monthly Notices of the Royal Astronomical Society* 358:1383–1393.
- Braatz A., Ott U., Henning T., Jäger C., and Jeschke G. 2000. Infrared, ultraviolet, and electron paramagnetic resonance measurements on presolar diamonds: Implications for optical features and origin. *Meteoritics & Planetary Science* 35:75–84.
- Bradley J. P., Keller L. P., Snow T. P., Hanner M. S., Flynn G. J., Gezo J. C., Clemett S. J., Brownlee D. E., and Bowey J. E. 1999. An infrared spectral match between GEMS and interstellar grains. *Science* 285:1716–1718.
- Brearly A. J. and Jones H. J. 1998. Chondritic meteorites. In *Planetary materials*, edited by Papike J. J. Washington D.C.: Mineralogical Society of America. pp. 31–370.
- Bregman J. D., Campins H., Witteborn F. C., Wooden D. H., Rank D. M., Allamandola L. J., Cohen M., and Tielens A. G. G. M. 1987. Airborne and groundbased spectrophotometry of comet P/Halley from 5–13 micrometers. *Astronomy and Astrophysics* 187:616–620.
- Bukovanská M., Nimec I., and Solc M. 1998. Study of some achondrites and chondrites by fourier-transformed infrared microspectroscopy and drifts (abstract). *Meteoritics & Planetary Science* 33:A25.
- Burns R. G. and Huggins F. E. 1972. Cation determination curves for Mg-Fe-Mn olivines from vibrational spectroscopy. *American Mineralogist* 57:967–985.

- Campins H. and Ryan E. V. 1989. The identification of crystalline olivine in cometary silicates. *The Astrophysical Journal* 341: 1059–1066.
- Chapman C. R. and Salisbury J. W. 1973. Comparisons of meteorite and asteroid spectral reflectivities. *Icarus* 19:507–522.
- Chihara H., Koike C., Tsuchiyama A., Tachibana S., and Sakamoto D. 2002. Compositional dependence of infrared absorption spectra of crystalline silicates. I. Mg-Fe pyroxenes. *Astronomy and Astrophysics* 391:267–273.
- Colangeli L., Henning T., Brucato J. R., Clément D., Fabian D., Guillois O., Huisken F., Jäger C., Jessberger E. K., Jones A., Ledoux G., Manicó G., Mennella V., Molster F. J., Mutschke H., Pirronello V., Reynaud C., Roser J., Vidali G., and Waters L. B. F. M. 2003. The role of laboratory experiments in the characterisation of silicon-based cosmic material. *Annual Review of Astronomy and Astrophysics* 11:97–152.
- Cooney T. F., Scott E. R. D., Krot A. N., Sharma S. K., and Yamaguchi A. 1998. Confocal raman microprobe and IR reflectance study of minerals in the Martian meteorite ALH 84001 (abstract #1332). 29th Lunar and Planetary Science Conference. CD-ROM.
- Dalton J. B. and Bishop J. L. 2003. Micro-spectroscopy as a tool for detecting micron-scale mineral variations across a rock surface: An example using a thin section of Martian meteorite ALH 84001. (abstract #2066) 34th Lunar and Planetary Science Conference. CD-ROM.
- Day K. A. 1976. Temperature dependence of mid-infrared silicate absorption (abstract). *The Astrophysical Journal* 203:L99.
- Deer W. A., Howie R. A., and Zussmann J. 1992. *An introduction to the rock-forming minerals*. Essex: Addison Wesley Longman. 696 p.
- Draine B. T. 2003. Interstellar dust grains. *Annual Reviews in Astronomy and Astrophysics* 41:241–289.
- Farmer V. C. 1974. *Infrared spectra of minerals*. Dorking, Surrey: Mineralogical Society. 539 p.
- Gaffey M. J. 1976. Spectral reflectance characteristics of the meteorite classes. *Journal of Geophysical Research* 81:905–920.
- Hanner M., Gehr R. D., Harker D. E., Hayward T. L., Lynch D. K., Mason C. C., and Russell R. W. 1997. Thermal emission from the dust coma of comet Hale-Bopp and the composition of the silicate grains. *Earth, Moon and Planets* 79:247–264.
- Hofmeister A. M. 1987. Single-crystal absorption and reflection infrared spectroscopy of forsterite and fayalite. *Physics and Chemistry of Minerals* 14:499–513.
- Hofmeister A. M., Xu J., Mao H.-K., Bell P. M., and Hoering T. C. 1989. Thermodynamics of Fe-Mg olivines at mantle pressures: Mid- and far-infrared spectroscopy at high pressure. *American Mineralogist* 74:281–306.
- Hofmeister A. M. 1997. Infrared reflectance spectra of fayalite, and absorption data from assorted olivines, including pressure and isotope effects. *Physics and Chemistry of Minerals* 24:535–546.
- Hofmeister A. M., Keppel E., Bowey J. E., and Speck A. K. 2000. Causes of artefacts in infrared spectra of powders (abstract #ESA-SP 456). ISO Beyond the Peaks: The 2nd ISO Workshop on Analytical Spectroscopy. p. 343.
- Jäger C., Molster F. J., Dorschner J., Henning T., Mutschke H., and Waters L. B. F. M. 1998. Steps towards interstellar silicate mineralogy. IV. The crystalline revolution. *Astronomy and Astrophysics* 339:904–916.
- Jones T. D., Lebofsky L. A., and Lewis J. S. 1989. Mid-IR reflectance spectra of carbonaceous chondrites: Applications to low-albedo asteroids (abstract). *Meteoritics* 24:282.
- Johnson T. V. and Fanale F. P. 1973. Optical properties of carbonaceous chondrites and their relationship to asteroids. *Journal of Geophysical Research* 78:8507–8518.
- Keller L. P., Bradley J. P., Bouwman J., Molster F. J., Waters L. B. F. M., Henning G. J. F. T., and Mutschke H. 2000. Sulfides in interplanetary dust particles: A possible match to the 23 μm feature detected by the infrared space observatory (abstract #1860). 31st Lunar and Planetary Science Conference. CD-ROM.
- Keller L. P., Hony S., Bradley J. P., Molster F. J., Waters L. B. F. M., Bouwman J., de Koter A., Brownlee D. E., Flynn G. J., Henning T., and Mutschke H. 2002. Identification of iron sulphide grains in protoplanetary disks. *Nature* 417:148–150.
- Keller L. P. and Flynn G. J. 2003. Far-IR spectroscopy of interplanetary dust, circumstellar silicate analogs, and aerogel: A prelude to stardust samples (abstract #1903) 34th Lunar and Planetary Science Conference. CD-ROM.
- Kessler M. F., Steinz J. A., Anderegg M. E., Clavel J., Drechsel G., Estaria P., Faelker J., Riedinger J. R., Robson A., Taylor B. G., and Ximenez de Ferran S. 1996. The Infrared Space Observatory (ISO) mission. *Astronomy and Astrophysics* 315:L27–L31.
- Koike C., Chihara H., Tsuchiyama A., Suto H., Sogawa H., and Okuda H. 2003. Compositional dependence of infrared absorption spectra of crystalline silicate II. Natural and synthetic olivines. *Astronomy and Astrophysics* 399:1101–1107.
- Maras A., Macri M., Ballirano P., Calvani P., Lupi S., Maselli P., Ruzicka B., Tobin M. J., and Chesters M. A. 2001. In situ synchrotron infrared reflectance study of olivine microcrystals in meteorite matrices (abstract). *Meteoritics & Planetary Science* 36:A121.
- Molster F. J., Waters L. B. F. M., and Tielens A. G. G. M. 2002. Crystalline silicate dust around evolved stars. II. The crystalline silicate complexes. *Astronomy and Astrophysics* 382:222–240.
- Molster F. J., Lim T. L., Sylvester R. J., Waters L. B. F. M., Barlow M. J. D., Beintema D. A., Cohen M., Cox P., and Schmitt B. 2001. The complete ISO spectrum of NGC 6302. *Astronomy and Astrophysics* 372:165–172.
- Molster F. J., Demyk A., D'Hendecourt L., and Bradley J. P. 2003. The first 2–50 μm infrared spectrum of an interplanetary dust particle (IDP) (abstract #1148). 34th Lunar and Planetary Science Conference. CD-ROM.
- Morlok A., Jones G. C., and Grady M. M. 2004. FT-IR Micro-spectroscopy of fine-grained planetary materials: Further results (abstract #1622). 35th Lunar and Planetary Science Conference. CD-ROM.
- Morlok A., Bowey J. E., Köhler M., and Grady M. M. Forthcoming. FT-IR microspectroscopy of planetary materials: Comparison of measurement techniques. *Planetary and Space Science*.
- Moroz L. V., Schmidt M., Schade U., Hiroi T., and Ivanova M. A. 2005. Synchrotron-based IR microspectroscopy as a useful tool to study hydration states of meteorite constituents. (abstract #1357). 36th Lunar and Planetary Science Conference. CD-ROM.
- Moss A. A., Hey M. H., Elliott C. J., and Easton A. J. 1967. Methods for the chemical analysis of meteorites: The major and some minor constituents of chondrites. *The Mineralogical Magazine* 36:101–119.
- Miyamoto M. 1992. Infrared diffuse reflectance spectra of several thermally metamorphosed carbonaceous chondrites (abstract). *Proceedings of the NIPR Symposium on Antarctic Meteorites* 5: 155–164.
- Miyamoto M. and Zolensky M. E. 1994. Infrared diffuse reflectance spectra of carbonaceous chondrites: Amount of hydrous minerals. *Meteoritics* 29:849–853.
- Osawa T., Kagi H., and Nagao K. 2001. Mid-infrared transmission spectra of individual Antarctic micrometeorites and carbonaceous chondrites. *Antarctic Meteorite Research* 14:71–80.

- Palomba E., Colangeli L., Esposito F., and Rotundi A. 2000. The infrared micro-spectroscopy technique: Application to the study of planetary solid compounds. *Società Astronomica Italiana* 71: 1139–1143.
- Raynal P. I., Quirico E., Borg J., Deboffle D., Dumas P., d'Hendecourt L., Bibring J.-P., and Langevin Y. 2000. Synchrotron infrared microscopy of micron-sized extraterrestrial grains. *Planetary and Space Science* 48:1329–1339.
- Sandford S.A. 1984. Infrared transmission spectra from 2.5 to 25 microns of various meteorite classes. *Icarus* 60:115–126.
- Salisbury J. W., Hunt G. R., and Lenhoff C. J. 1975. Visible and near-infrared spectra. X-Stony meteorites. *Modern Geology* 5:115–126.
- Salisbury J. W., D'Aria, Dana M., and Jarosewich E. 1991. Midinfrared (2.5–13.5 microns) reflectance spectra of powdered stony meteorites. *Icarus* 92:280–297.
- Salisbury J. W., Walter L. S., Vergo N., and D'Aria D.M. 1992. *Infrared (2.1–25 μ m) spectra of minerals*. Baltimore, Maryland: The John Hopkins University Press. 267 p.
- Sitko M. L., Grady C. A., Lynch D. K., Russell R. W., and Hanner M. S. 1999. Cometary dust in the debris disks of HD 31648 and HD 163296: Two “baby” pictoris stars. *The Astrophysical Journal* 510:408–412.
- Speck A. K., Barlow M. J., Sylvester R. J., and Hofmeister A. M. 2000. Dust features in the 10 μ m infrared spectra of oxygen-rich evolved stars. *Astronomy and Astrophysics* 146:437–464.
- Tarantino S. C., Carpenter M. A., and Domeneghetti M. C. 2003. Strain and local heterogeneity in the forsterite-fayalite solid solution. *Physics and Chemistry of Minerals* 30:495–502.
- Tarte P. 1965. Experimental study and interpretation of infrared microspectroscopy techniques: Application to the study spectra of silicates and germanates. *Mémoire de la Classe des Sciences*. Academic Royal Belgian Society. Series 8, vol. 35, parts 4a and 4b.
- Waelkens C., Waters L. B. F. M., de Graauw M. S., Huygen E., Malfait K., Plets H., Vandenbussche B., Beintema D. A., Boxhoorn D. R., Habing H. J., Heras A. M., Kester D. J. M., Lahuis F., Morris P. W., Roelfsema P. R., Salama A., Siebenmorgen R., Trams N. R., van der Blik N. R., Valentijn E. A., and Wesselius P. R. 1996. SWS observations of young main-sequence stars with dusty circumstellar disks. *Astronomy and Astrophysics* 315:L245–L248.
- Waters L. B. F. M., Molster F. J., de Jong T., Beintema D. A., Waelkens C., Boogert A. C. A., Boxhoorn D. R., de Graauw T., Drapatz S., Feuchtgruber H., Genzel R., Helmich F. P., Heras A. M., Huygen R., Izumiura H., Justtanont K., Kester D. J. M., Kunze D., Lahuis F., Lamers H. J. G. L. M., Leech K. J., Loup C., Lutz D., Morris P. W., Price S. D., Roelfsema P. R., Salama A., Schaeidt S. G., Tielens A. G. G. M., Trams N. R., Valentijn E. A., Vandenbussche B., van den Ancker M. E., van Dishoeck E. F., van Winckel H., Wesselius P. R., and Young E.T. 1996. Mineralogy of oxygen-rich dust shells. *Astronomy and Astrophysics* 315:L361–L364.
- Wooden D. H., Woodward C. E., and Harker D. E. 2004. Discovery of crystalline silicates in comet C/2001 Q4 (NEAT). *The Astrophysical Journal* 612:L77–L80.
- Zaikowski A. and Knacke R. F. 1975. Infrared spectra of carbonaceous chondrites and the composition of interstellar grains. *Astrophysics and Space Science* 37:3–9.